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INVESTIGATION OF INFRARED SPECTRA OF ATMOSPHERIC GASES
TO SUPPORT STRATOSPHERIC SPECTROSCOPIC INVESTIGATIONS

John H. Shaw
Department of Physics

For the Period
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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546

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June, 1980



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INTRODUCTION

Progress in our investigations of the infrared spectra of atmospheric gases to support stratospheric spectroscopic investigations is described.

The information concerning the atmosphere which can be obtained by spectroscopy depends on the nature of the instrumentation and our knowledge of the absorption characteristics of atmospheric gases. One of the characteristics common to many of the spectroscopic stratospheric experiments currently being considered is the improvement in the spectral resolution compared with earlier investigations. As the spectral resolution approaches the widths of absorption lines there is a large increase in the amount of atmospheric information contained in the data. However, in order to extract this information, the parameters (position, intensity, shape) of the spectral lines must be known with sufficient accuracy.

Concern has been expressed regarding the adequacy of our knowledge of these parameters at a number of meetings of spectroscopists held during the past year (1). At the present, much of this concern is qualitative in nature. Part of the effort carried out under this grant has been to investigate analytical methods which will allow some of these problems to be studied more quantitatively. On the one hand, it is necessary to specify the accuracy required of the line parameters to retrieve atmospheric information with the precision desired; on the other hand, it is useful to be able to estimate the ranges of atmospheric conditions (e.g., the vertical depths in the atmosphere) over which information can be obtained with a given instrument design. It is not our purpose to pursue this problem extensively. We do consider it to be important and that it has received less consideration than needed in evaluating the usefulness of different experiments.

The spectroscopy workshops have emphasized that more information is required about the absorbing properties of many atmospheric gases over wide spectral ranges and for large numbers of spectral lines. Usually, this information is obtained by making measurements on individual lines. We are developing methods of simultaneously analyzing entire bands containing many lines. During the past few months these methods have been applied to the analysis of bands of N₂O and CO₂. Progress in this analysis is reported.

EXPERIMENTAL INVESTIGATIONS

(Hoke, Hawkins, Nordstrom, Damon)

The principal apparatus used in our investigations consists of a Nicolet Fourier Transform Spectrometer and a 10m multiple traversal cell. This system was brought into operation during the first year of this grant.

The transfer optics between the source, interferometer, absorption cell, and detector can be flushed with nitrogen and partially evacuated. This allows much of the atmospheric H₂O and CO₂ in the path to be removed. Two detectors are available. A Hg Cd Te, extended-range detector enables spectra to be collected from approximately 800 cm⁻¹ to beyond 6000 cm⁻¹. An In Sb detector, with greater detectivity, can be used from 1900 cm⁻¹ to higher frequencies. Spectra, with a resolution of about 0.05 cm⁻¹, of O₃, CO₂, N₂O, H₂O and a number of other gases have been obtained. A gas handling system which allows precisely measured, small samples of gases to be introduced into the cell has recently been added to the cell. In addition, a tape recorder was integrated with the Nicolet system so that spectra can now be stored on tape. Other improvements to the system have included the writing of programs to be used with the Nicolet system which allow the spectra to be plotted in different formats. However, many of the programs for spectral analysis require the use of the main Ohio State University computing system. We were fortunate in obtaining the assistance of Arthur Levitt, who prepared programs which allowed this system to read the tapes of spectra. These programs were written in January, 1980. Since then it has been possible to begin the detailed analysis of some of the spectra. These analyses have revealed problems with frequency calibration. The line frequencies (cm⁻¹) are based on the frequency of the laser which controls the interferometer drive. The laser supplied by Nicolet was found to be insufficiently stable to operate over the long optical retardations required to obtain high resolution spectra. A mode-locked laser has now been installed. This provides the required stability but its frequency has not been established accurately. In addition, small frequency shifts occur in spectra recorded at different times. We are investigating the best method of frequency calibration.

SPECTRAL ANALYSIS

SPECTRUM PLOTTING AND LINE FINDING PROGRAM (Hawkins, Nordstrom)

A computer program has been written to plot spectra and to estimate the positions of absorption lines. An example of the output of this program is shown in Fig. 1.

This program reads the spectrum from magnetic tape, written by the Nicolet minicomputer used to acquire and transform the interferogram. A quartic spline interpolation is used to improve the appearance of the spectrum. The interpolated spectrum is searched by a line finder subroutine; the line centers found by this routine are indicated by tic marks at the top of the plotted spectrum. The estimated frequencies of the line centers are listed on the same plot. For spectra such as the one shown, the estimated frequencies of the line centers have a precision of about $\pm 0.003 \text{ cm}^{-1}$. The line finder subroutine uses an externally supplied estimate of the signal-to-noise ratio to reject noise dips.

This subroutine finds the great majority of lines and almost never finds spurious lines. It has become a standard aid to analysis in this laboratory, and we have already received requests from other researchers for copies of the subroutine.

CALCULATION OF SYNTHETIC SOLAR SPECTRA

(Niple, Shaw, Shaffer)

During the first year's effort, E. Niple prepared a program for calculating synthetic solar spectra. This program is described in an Interim Technical Report (2) issued under this grant. The program incorporates a ray tracing program described by Snider and Goldman (3) and an efficient method of calculating spectra with Voigt-shaped lines. Dr. Niple is now a post-doctoral Fellow at NCAR and has since improved the program further. He has used it, together with a nonlinear, least squares technique (NLLS) to analyze solar spectra obtained by Murcray et al. (4) with a balloon-borne FTS, to obtain profiles of stratospheric NO_2 and H_2O .

A graduate student, William Shaffer, spent part of the summer of 1979 becoming acquainted with this program, and he expects to continue this work during the summer of 1980. It is hoped that these investigations will lead to better estimates of the accuracy required in line parameters to interpret stratospheric spectroscopic investigations. [Niple et al. (4) have found that the accuracy of their NLLS analysis of solar spectra was affected by errors in the positions of the lines analyzed.] It is also hoped that these investigations may allow more

1200.068	1200.268	1200.408	1200.530	1200.918	5
1201.143	1201.268	1201.772	1202.015	1202.133	10
1202.618	1202.886	1202.990	1203.462	1203.753	15
1203.039	1204.303	1204.616	1204.700	1205.142	20
1205.470	1205.553	1205.975	1206.326	1206.410	25
1206.810	1207.178	1207.256	1207.645	1208.031	30
1208.098	1208.463	1208.878	1209.294	1209.728	35
1210.125	1210.573	1210.941	1211.420	1211.755	40
1212.257	1212.504	1213.089	1213.373	1213.922	45
1214.185	1214.753	1214.986	1215.576	1215.780	50
1216.039	1216.400	1216.584	1216.930	1217.222	55
1217.387	1217.814	1218.040	1218.184	1218.705	60
1218.856	1218.976	1219.673	1219.761	1220.540	

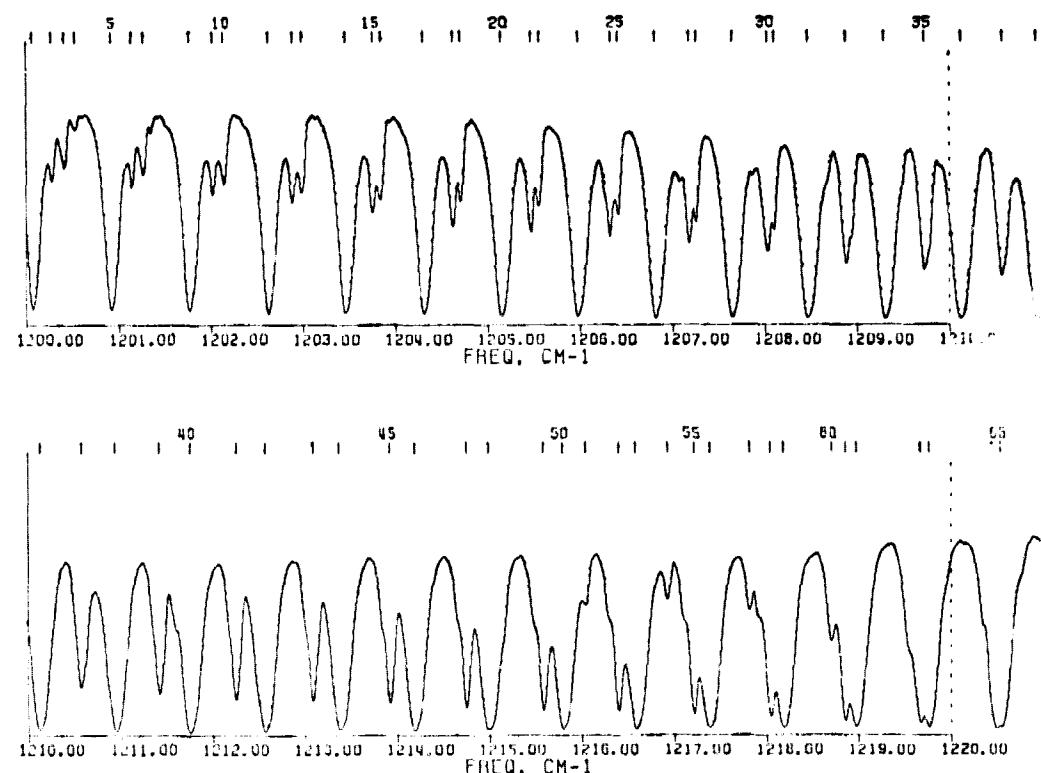


Fig. 1. Output of ATLAS program -- portion of N_2O spectrum.

quantitative estimates of the precision with which atmospheric information (temperature density, constituent profiles, etc.) can be obtained from spectra. Methods for this type of analysis are still in an embryonic stage although some preliminary ideas have been discussed by Nippe et al. (2, 5, 6).

NLLS ANALYSIS OF SPECTRA (Lin, Shaw)

C. L. Lin was associated with this project from January--November, 1979. During this period an NLLS method for analyzing Voigt-shaped lines was completed. This work has now been published (7). In addition a new NLLS technique of whole band analysis was demonstrated (8). Unlike conventional methods which require estimates of line positions, the entire spectrum is used as the experimental data to be analyzed. It is necessary to provide models for the band parameters which describe the positions, the intensities, and widths of the lines. The adjustable parameters in these models are then determined directly. Application of this technique to the analysis of bands of HCl and CO demonstrated that the important band parameters could be determined with high precision. The samples of HCl and CO, whose spectra were analyzed, were near atmospheric pressure and the shapes of the lines were assumed to be Lorentzian. Although the method is simple in concept, a number of difficulties were encountered in its application. In particular, the programs required large amounts of computer time, and, if many parameters are to be determined simultaneously, good initial guesses of their values are required if the program is to converge in a small number of iterations. It also became clear that a single spectrum contained a finite amount of information about the band parameters. For example, the positions of narrow spectral lines can be estimated more precisely than wider lines. On the other hand, if the line width is smaller than the spectral resolution, the values of the line widths cannot be estimated precisely.

This leads to interesting problems in experiment design, similar to, but more complicated than, those discussed by Nippe and Shaw (5, 6). It is not planned to pursue this further at this time, although they have recurred in the work of Hoke and Hawkins described below.

SPECTRA OF O₃

A number of spectra of ozone were obtained in the fall of 1979. These covered the region from 800 to 5000 cm⁻¹ and were obtained with the Hg Cd Te detector. Samples of these spectra were sent to A. Barbe (Reims) and C. Camy-Peyret (Orsay) who recognized that the line positions were systematically shifted because of the calibration problems noted earlier. It is planned to obtain additional spectra

when this calibration problem is better resolved. Although laboratory O₃ spectra are important for many stratospheric investigations, it is more useful if line parameters are obtained. These can be estimated by NLLS analysis of entire bands, but we have not applied this technique to complicated spectra such as O₃. Before tackling O₃ spectra, we believe it is important to study the applications to relatively straightforward spectra such as CO₂ and N₂O as described below.

ANALYSIS OF CO₂ SPECTRA (Hoke, Shaw)

Nonlinear least squares analysis has been used to obtain simultaneous estimates of band parameters which account for the appearance of an entire absorption band or bands. An example is the analysis of an absorption band of CO by Lin and Shaw (8).

For the present study of bands of CO₂ the parameters to be estimated and the expressions in which they are included are listed in Table 1. The transmittance, I(ν), at a particular frequency ν (cm⁻¹) depends on the background B(ν), which is usually expressed as a polynomial in ν with several coefficients to be estimated; a symmetric instrument function $\sigma(\nu, H)$ with one parameter, the resolution H, to be estimated; the quantity $\exp(-K(\nu) \cdot U)$, which is the expression for the value of the monochromatic transmittance at ν when several lines are present.

The instrument function may take several forms; e.g., triangular, gaussian, sinc, etc. For unapodized data, the sinc function is the most appropriate form.

The absorption coefficient K(ν) will differ in analytical form depending upon the line shape assumed. In this work a Lorentzian shape is used.

The absorption coefficient K(ν) is a function of the line positions ν_j which depend on estimates of ν_0 , the band center; rotational constants B', B'', D', D'', H', H''; line intensities, S(M) which depend on estimates of C₀, Herman Wallis factors β_1 and β_2 ; E (B'', D'', H''); half widths $\alpha(M)$ which are expressed as a simple polynomial in M with the α_i to be estimated.

The algorithm used to perform the regression has been described by Ralston and Jennrich (9). While various nonlinear regression algorithms achieve the same end in different ways, they are basically the same; i.e., the sum of squared differences (residual sum of squares, RSS) between the observed data and predicted data calculated by using values of the parameters to be estimated is minimized by adjusting the values of the parameters (8).

The absorption bands being considered are those of naturally occurring isotopic CO₂ at 2600 cm⁻¹ of 177 torr, 450 meter homogeneous

path (Fig. 2). The notation in Fig. 2 is that of McClatchey et al. (10). The strongest band, centered near 2614 cm^{-1} , is blended, in both the P and R branches, by weaker bands centered near 2618 cm^{-1} and 2641 cm^{-1} .

Band parameters for two of the three bands in the region have been obtained by analyzing each band separately. The strongest of the three bands was analyzed first and its parameters were then fixed to allow each weaker band in turn to be analyzed. The estimates obtained for the two bands centered at 2614 cm^{-1} and 2641 cm^{-1} by this fix-one-band-free-one-band technique are listed in Table 2. The notation is that of Table 1. The numbers in parentheses are the standard deviations or estimated uncertainties of the last significant figure present.

Analysis of the stronger band was performed with approximately 60 P and 60 R branch lines. The weaker band was analyzed with approximately 45 P and 45 R branch lines. The half-widths for the weaker band were assumed to be the same as those of the stronger band.

For comparison, values of some of these parameters from a tabulation by Rothman and Benedict (11) are listed in Table 3. In addition, the predicted spectrum is compared with the observed spectrum in Figs. 3 and 4 which show segments of the region being considered (see Fig. 1). The upper portions of both figures show the synthetic spectra, calculated by using quantities from Table 2, displaced and above the observed spectra. The lower portions show the differences between the calculated and observed data, plotted on a scale expanded by a factor of five compared to the scale in the upper portion (notice the unmodeled P branch line, on the two scales, at approximately 2614.5 cm^{-1} in Fig. 2).

Throughout the region, the agreement between the calculated and observed data is fairly good.

Of particular interest are half-widths, which are shown as a function of M in Fig. 5, corrected to $P = 760 \text{ Torr}$. M is equal to $-J$ in the P branch and to $J + 1$ in the R branch. Qualitatively, these widths agree with experimental results of other investigators. In particular the value of $\alpha_0 = 0.13 \text{ cm}^{-1}$ agrees with small M values from other studies (12, 13). Also, even though the uncertainties for α_1 and α_2 are large, they are determined with sufficient precision to predict that the half-widths decrease with M and to a value, for $M = 60$, which agrees with Drayson et al. (13). That the detailed functional dependence of α on M is missing is a result of using an inadequate model, in this case a simple three-term polynomial. It is planned to improve the model by including more terms or by choosing different, more appropriate powers of M.

In addition to parameter estimates and estimates of uncertainty or standard deviation, the regression analysis produces estimates of linear correlation among the parameters being simultaneously estimated.

TABLE I. EXPRESSIONS USED TO MODEL ABSORPTION SPECTRA

$$I(v) = \int B(v) \cdot \sigma(v-v') \cdot \exp(-K(v) \cdot v) dv' / \int \sigma(v-v') dv'$$

$$K(v) = \sum_j S_j \alpha_j / \pi ((v-v_j)^2 + \alpha_j^2) \quad v = E' - E$$

$$E' = v_0 + B(J(J+1) - L^2) - D(J(J+1) - L^2)^2 + H(J(J+1) - L^2)^3$$

$$E = B(J(J+1) - L^2) - D(J(J+1) - L^2)^2 + H(J(J+1) - L^2)^3$$

$$S(M) = C_0 (1 + \beta_1 M + \beta_2 M^2) \cdot \nu(M) \cdot |M| \cdot \exp(-E(M)/kT)$$

$$C_0 = 8 \pi^3 |R|^2 / 3 \hbar c Q$$

$$\alpha(M) = \alpha_0 + \alpha_1 |M| + \alpha_2 |M|^2 + \alpha_3 |M|^3$$

$$\alpha = \alpha_R |P/P_R|$$

TABLE 2. Estimated band constants for absorption bands near 2614 cm⁻¹ and 2641 cm⁻¹.

v_0	2614.2531(1)	v_0	2641.243(1)
B'	0.367739(1)	B'	0.37805(4)
B''	0.368181(1)	B''	0.37861(4)
D'	1.109(7) $\times 10^{-7}$	D'	1.3(2) $\times 10^{-7}$
D''	1.209(6) $\times 10^{-7}$	D''	1.3(2) $\times 10^{-7}$
a_0	2.99(3) $\times 10^{-2}$	c_0	6.7(1) $\times 10^{-31}$
a_1	-6.2(3) $\times 10^{-5}$		
a_2	-2.6(6) $\times 10^{-6}$		
β_1	8(2) $\times 10^{-5}$		
c_0	1.5607(3) $\times 10^{-29}$		

TABLE 3. Band constants for absorption bands near 2614 cm⁻¹ and 2641 cm⁻¹ reported by Rothman and Benedict(4).

B'	0.367807	B'	0.37814
B''	0.368184	B''	0.3786143
D'	1.04 $\times 10^{-7}$	D'	1.18 $\times 10^{-7}$
D''	1.185 $\times 10^{-7}$	D''	1.2521 $\times 10^{-7}$

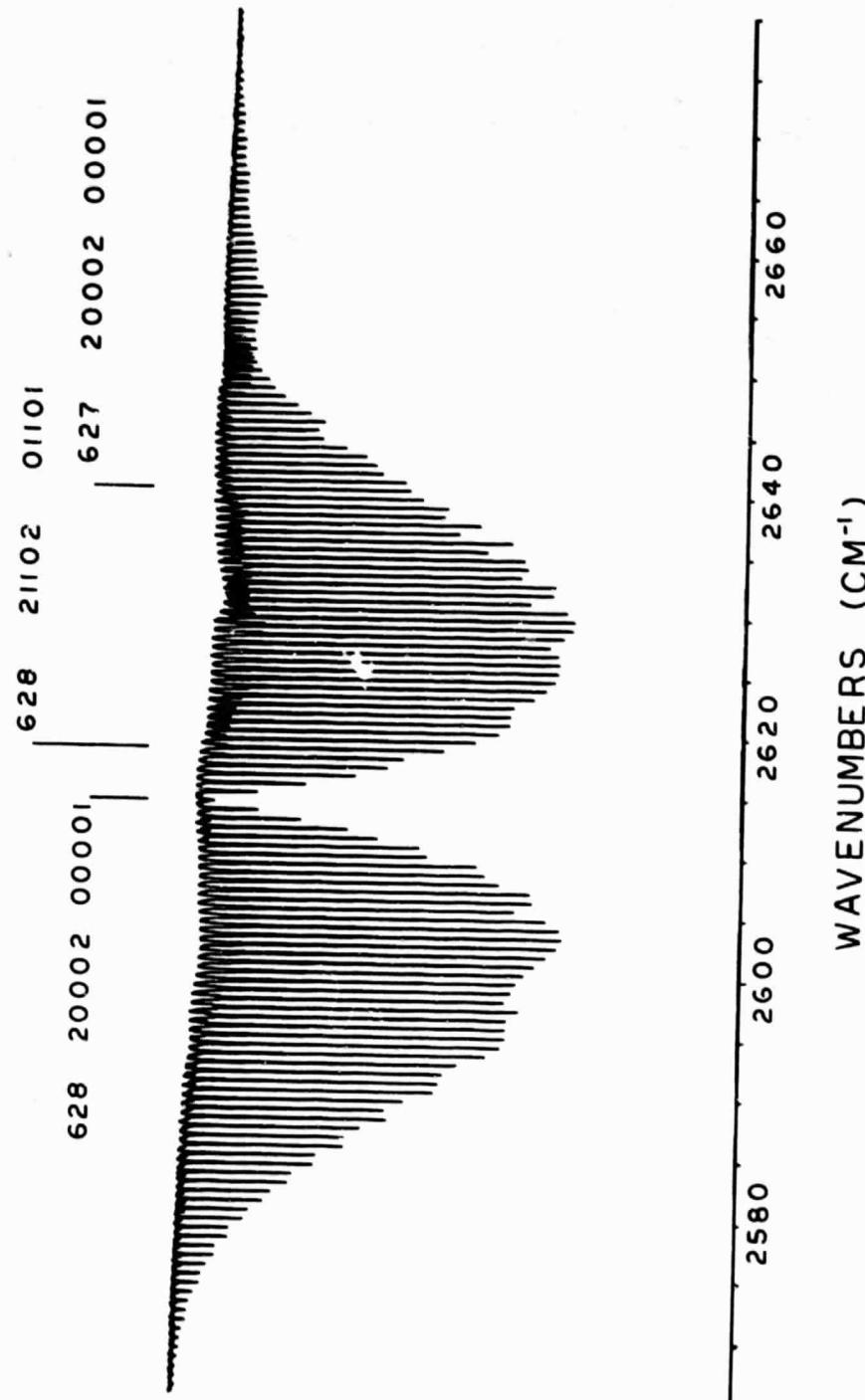


Fig. 2. Spectra of naturally occurring CO_2 near $3.8 \mu\text{m}$ including bands of $^{16}_{\text{O}}\text{C}^{18}_{\text{O}}$ near 2414 cm^{-1} and 2618 cm^{-1} and $^{16}_{\text{O}}\text{C}^{17}_{\text{O}}$ near 2641 cm^{-1} .

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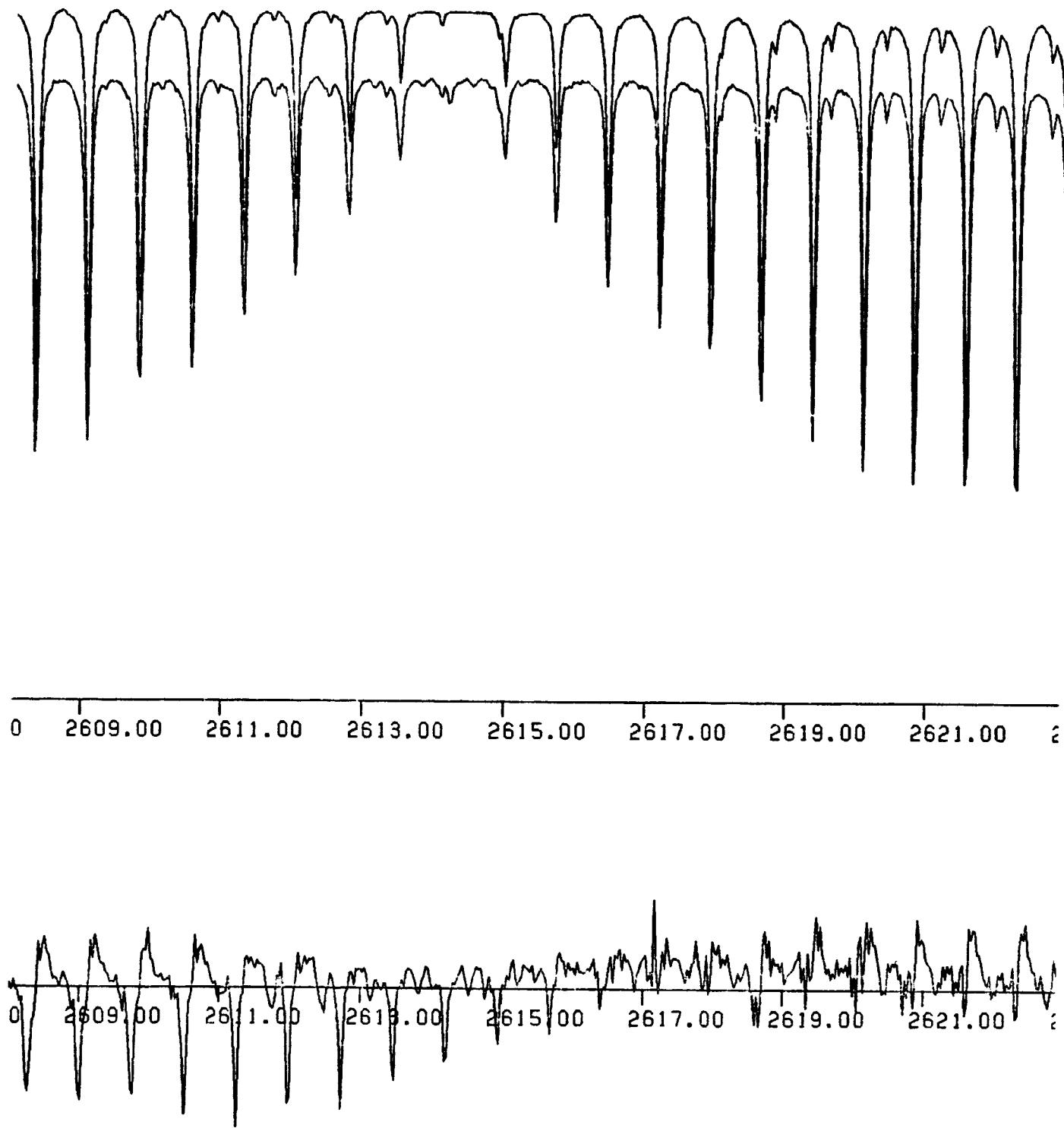


Fig. 3. Calculated and observed spectra near 2614 cm^{-1} . Upper spectra, upper portion is calculated, lower spectra observed. Lower portion is difference between observed and calculated.

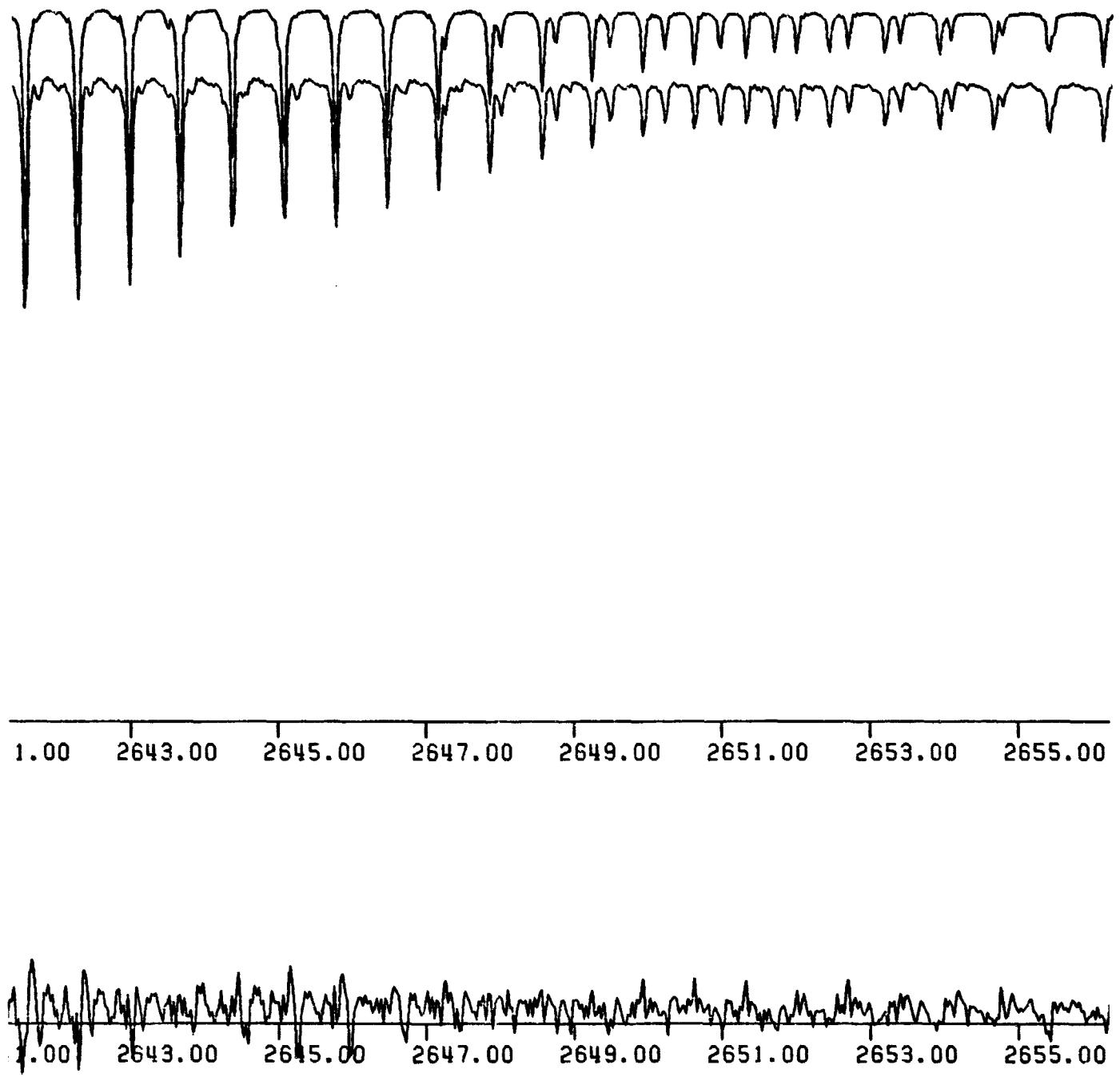


Fig. 4. Calculated and observed spectra near 2650 cm^{-1} . Upper spectra, upper portion is calculated, lower spectra observed. Lower portion is difference between observed and calculated.

4

HALFWIDTH

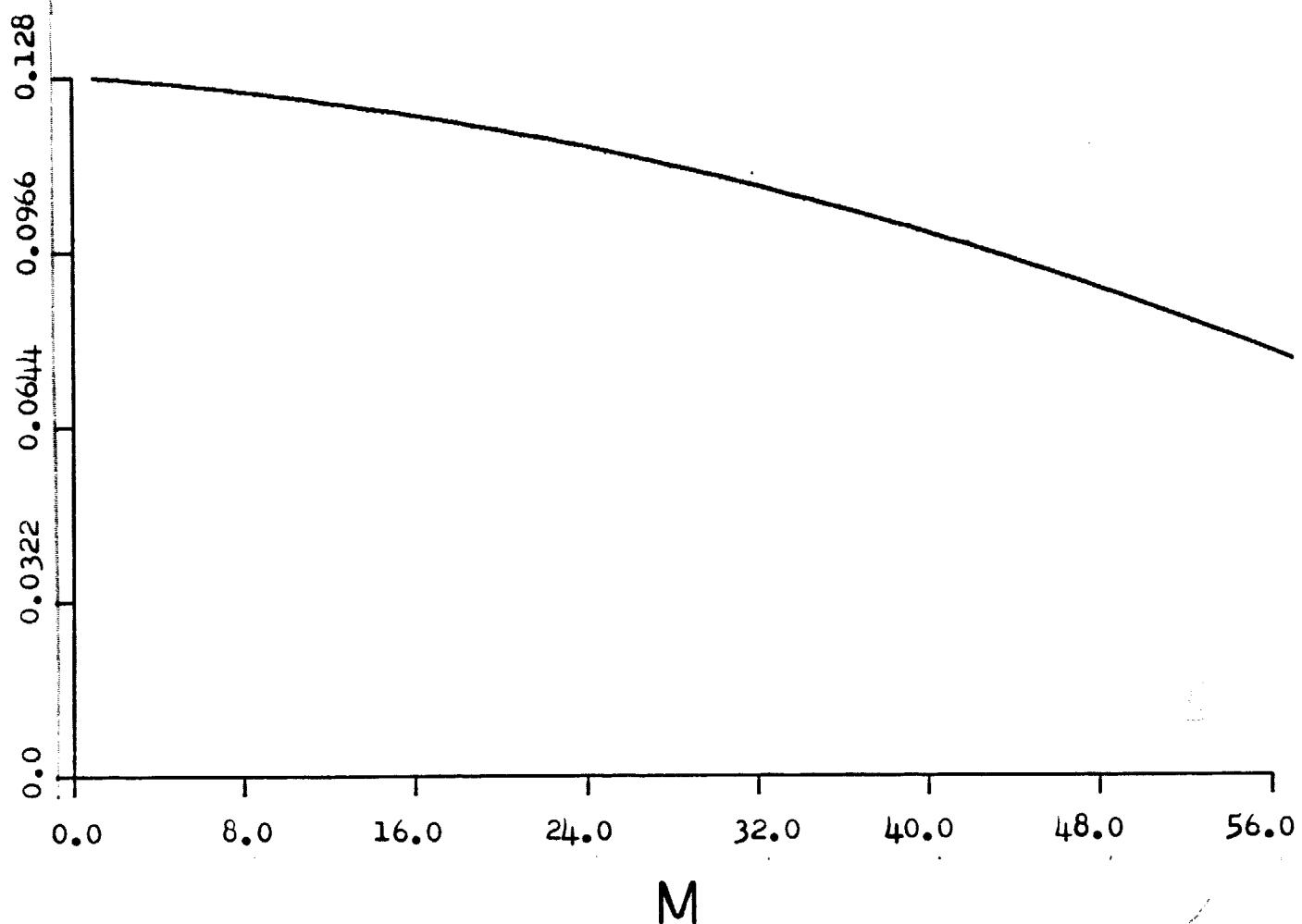


Fig. 5. Variation of line width with $|M|$ at $T=296$ K, $P=760$ Torr.

Part of the correlation matrix for the analysis of the strong 2614 cm⁻¹ band is reproduced in Table 4. Each entry is the linear correlation coefficient between the parameter to the left and the one at the top of the column. B_1 , B_2 , B_3 are the coefficients of the polynomial expression for the background and H is the instrument function width. ν_0 is the band center and the remaining parameters are those of Table 1.

The background parameters and instrument function width are quantities which one is obliged to estimate for a complete analysis of an absorption band but are of no intrinsic interest in this particular study. Table 4 shows that these quantities B_1 , B_2 , B_3 , H are relatively uncorrelated with the other quantities being estimated. This is what one would expect; the information pertaining to the background and instrument function can be separated from that for the rest of the parameters.

WHOLE-BAND ANALYSIS OF N₂O

A computer program has been developed to perform whole-band analysis of spectra of N₂O or similar molecules, using nonlinear least-squares spectral curve fitting. Fig. 6 shows a portion of a spectrum analyzed with this program. The bottom curve is the observed spectrum (the calculated spectrum is raised above it by 10% for clarity) and the top curve is the difference between calculated and observed multiplied by five.

In this program, estimates of spectral band parameters are obtained by performing a nonlinear regression on the observed spectrum. The program that performs the regression is PAR, one of the BMDP series of programs (14). PAR adjusts a set of band parameters so as to minimize the difference between the observed spectrum and the spectrum calculated from the band parameters.

The spectrum-calculating subroutine uses well-known models to calculate line parameters from the band parameters. It then calculates the spectrum using a Voigt line shape and a Gaussian instrument profile. It can be adapted to any molecule for which line parameters can be adequately calculated from band parameters.

The parameters estimated include:

line positions: B , D , H for upper and lower state of each band; ν_0 of upper state.

line intensities: one parameter proportional to the rotationless dipole matrix element and two Herman-Wallis factors, for each band.

line widths: three coefficients of a quadratic in J .

TABLE 4. Portion of correlation matrix from analysis of absorption band near 2614 cm⁻¹.

	B ₁	B ₂	B ₃	H
B ₁	1.0000			
B ₂	0.2645	1.0000		
B ₃	-0.6835	-0.5250	1.0000	
H	-0.1242	-0.1227	-0.0141	1.0000
v ₀	0.1603	0.0630	-0.2246	-0.0409
B'	-0.3133	-0.0321	0.2029	-0.1093
B''	-0.3066	-0.0331	0.1723	-0.1812
D'	-0.0369	-0.0773	0.0200	-0.3682
D''	0.0130	-0.0717	-0.0403	-0.4315
α_0	-0.0877	-0.1100	0.2187	0.2393
α_1	0.1716	0.1568	-0.3145	-0.0974
α_2	-0.1863	-0.1480	0.3353	0.1019
β_1	0.0477	-0.1381	-0.0274	-0.3971
C ₀	0.1720	0.0606	0.2013	-0.7603

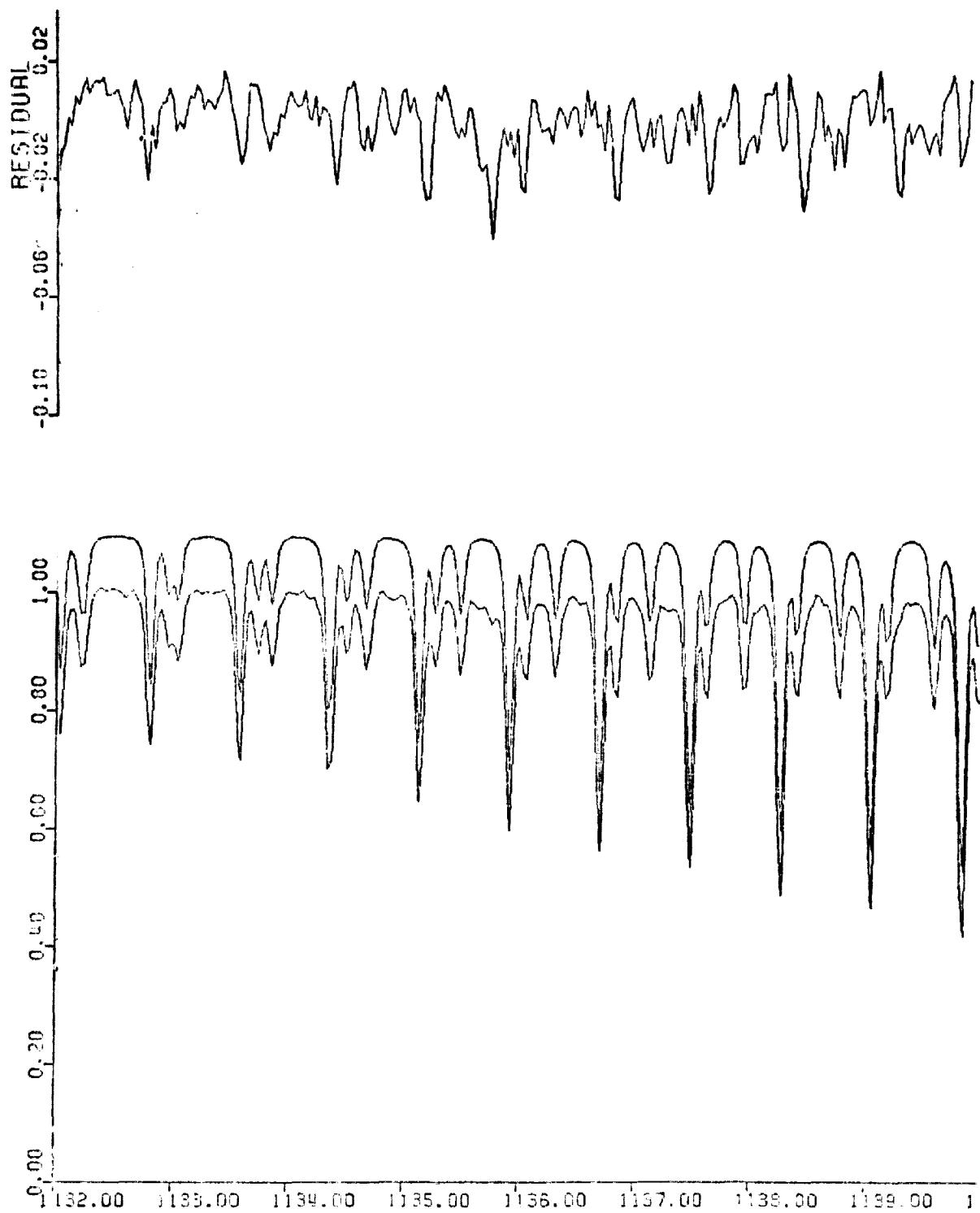


Fig. 6. Portion of a spectrum of $^{14}\text{N}_2\text{O}$ Nitrogen - Broadened to 200 Torr. Bottom curve -- observed spectrum. Middle curve -- fitted spectrum, +.10. Top curve -- observed - fitted, $\times 5$.

instrument function: resolution half-width.

background: coefficients of a polynomial in frequency,
as many as necessary.

For the spectrum which is illustrated in Fig. 6, which covers 100 cm^{-1} , includes more than 3000 data points and 200 lines belonging to the $2\nu_2$ (the stronger band) and the $3\nu_2 - \nu_2$ (the weaker δ -doubled band), 31 parameters were estimated.

While this program is not yet in its final form, the results so far have been as encouraging as could have been expected. In particular, the program has proven surprisingly good at simultaneously determining the instrument and line widths, which was expected to be the most difficult problem. For example, spectra taken at 10 torr were analyzed, in which the line width was much less than the resolution; also spectra at 200 torr, in which the line widths were comparable to the resolution. The retrieved values for the resolution did not differ by more than a few percent. The retrieved line widths, for the stronger lines, were within about 5% of those listed in the AFGL line listing for the $2\nu_2$ band of N_2O .

The major cause of discrepancies between the observed and calculated spectra are due to the use of a Gaussian instrument function in the calculation, rather than the real apodized instrument function. (The differences between a Gaussian and the unapodized $\sin(x)/x$ instrument function are so great that unapodized spectra cannot be adequately analyzed with a Gaussian.) The spectrum calculating sub-routine has been modified to include an arbitrary instrument function. While the computing time will be significantly increased, this is necessary to take full advantage of the spectral curve fitting technique's capabilities.

The analysis of a spectrum such as the one illustrated in Fig. 6, and described above, requires about 150 minutes of CPU time on the Amdahl/470 at the Instruction and Research Computer Center at Ohio State University, or about \$1,000 in computing money. The time is distributed over five or six runs in which selected subsets of parameters are allowed to vary, the remainder being fixed at initial or intermediate values. Such an analysis has been performed, from raw spectrum to final result, in one to two days of wall-clock time.

The current version of the program occupies two megabytes of memory. Other minimization routines are being investigated for analysis of larger amounts of data. However, PAR has proven to be effective and consistent, and the current version should be useful for analysis of spectra not much more than 100 cm^{-1} in extent and containing three or four bands.

ANALYSIS OF SINGLE LINE SPECTRA (Hoke, Shaw)

Nippe and Shaw (5) have discussed the dependence of the information about the parameters of Lorentz-shaped lines on the appearance of the spectrum. In this paper, a method of estimating the precision with which a given parameter, such as the line width, could be obtained, was described. No discussion concerning the correlations between parameter estimates or of the expected distributions of the estimates of the parameters and their standard deviations was given.

Because of our extensive use of NLLS analysis, we have been concerned about the nature of the results obtained by these methods. In order to investigate them further we have continued our investigation of a single Lorentz-shaped line. A synthetic spectrum of a single line was calculated extending about ten observed line widths on each side of the line and for about 100 signal values. Noise was simulated by adding random numbers with a Gaussian distribution to give an SNR of 100. A NLLS analysis was employed to give estimates of the background spectral resolution, and the line position, intensity and width. This was repeated 200 times with a different set of added noise (SNR = 100 in all cases). We have examined the parameter estimates and have found that the correlations between estimates obtained "experimentally" agree with those estimated by the NLLS program and that the parameter estimates and estimates of the standard deviations appear to be essentially normally distributed. These results will be described at the Infrared Symposium, Columbus, June 1980 and it is planned to prepare them for publication.

FUTURE PLANS

During the next few months, the major efforts will be the continuing analysis of bands of CO₂ and N₂O by NLLS. We expect that the experience gained during the past four months will allow the speed of analysis to be increased considerably. So far only the data in about a 100 cm⁻¹ interval in a single spectrum have been analyzed at one time. It is expected that simultaneous analysis of several regions containing bands with common levels or simultaneous analysis of the data on the same band from more than one spectrum will improve the precision of the parameter estimates. It may be possible to perform such analysis if satisfactory NLLS programs can be found which require less memory than the present program.

The principal thrust of these analyses will be first to identify the observed bands and obtain the parameters describing the line positions. Once this has been accomplished, it is expected that the half-widths and line intensities can be obtained with little further effort. We expect

to obtain both self-broadened and N₂-broadened line widths and to explore their dependence on temperature. If the opportunity occurs, we will also try to obtain more information concerning the line shapes, especially in the wings of the lines.

Naturally occurring CO₂ and N₂O contain a number of isotopic species. Spectrum of isotopically enriched samples will also be collected and analyzed if it is found necessary.

Further efforts will be made on improving the frequency calibration of the system.

It is planned to obtain spectra of O₃ at a variety of path lengths, temperatures, and total pressures.

As time permits we will continue our analysis of synthetic solar spectra to obtain a better understanding of the information contained in such spectra and to determine the type of laboratory investigations most urgently needed for their analysis.

During our analysis of N₂O and CO₂ bands we have found that sets of parameter estimates can be obtained by NLLS, all of which give essentially the same descriptions of the spectrum analyzed but with different parameter estimates. We are faced with making decisions about which of these sets best describes the molecular contents of these gases, but have not yet established suitable criteria. This problem appears to have connections with the analyses of Nippe and Hoke described above.

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